RESEARCH REPORT

(to protect the scientific priority, only published results are presented here)

January 2012 – December 2014

New Organometallic Compounds of Heavy Group 15 Metals (Antimony, Bismuth) -- Potential Use in Catalysis

PN-II-ID-PCE-2011-3-0933

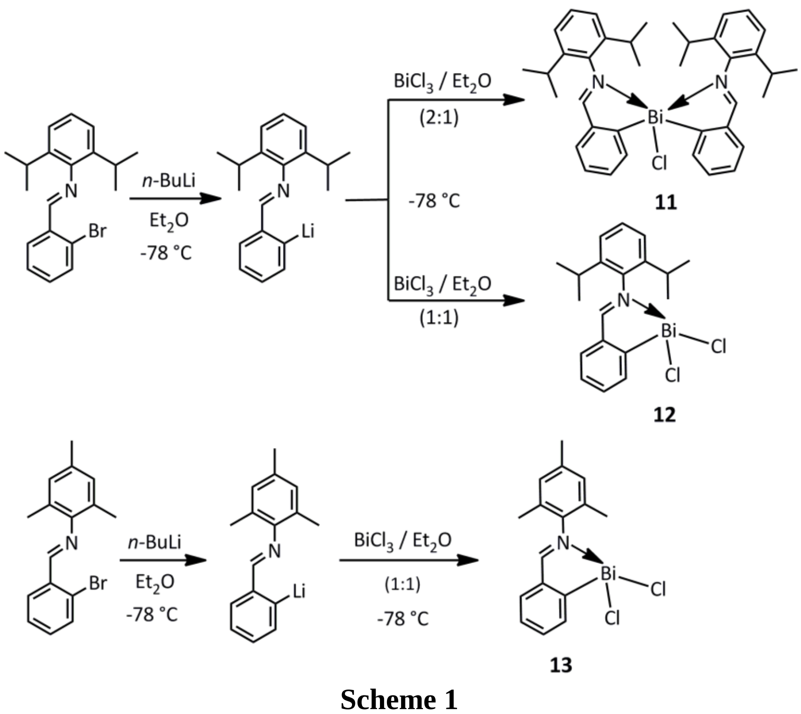
In the three year phases of the project fulfilled so far (Jan.-Dec. 2012, Jan.-Dec. 2013, and Jan.-Dec. 2014), besides current management activities (acquisition of reagents, solvents and other materials, small equipments), a new research laboratory for organometallic chemistry was arranged. In addition, in 2012 was accomplished an exhaustive literature search covering the topic intended to be developed within the project, an activity which resulted in a review published in a high ranked international journal.[1] Part of the results obtained so far within this project were included and presented as invited conferences (C2, C4 and C5 on the list of contributions to national and international conferences).

Phase Jan.-Dec. 2012

Chiral organometallic compounds (Sb, Bi) with organic ligand bearing one or two pendant arms

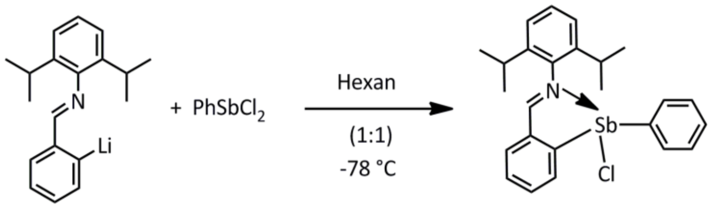
For the compounds intended to be investigated within this project the chirality can arise due to different reasons, *e.g.* (*i*) the organic ligand has a chiral carbon atom or heteroatom; (*ii*) the metal atom is chiral due to the presence of three different substituents attached to it; (*iii*) induced chirality at the metal centre through intramolecular coordination,[1,2] etc.

The studies concerning the organoantimony(III) compounds with ligands of type 2-(2',6'-$^{i}Pr_2C_6H_3N{=}CH)C_6H_4$ and 2-(2',4',6'-$Me_3C_6H_2N{=}CH)C_6H_4$, in part accomplished within the previous research project (PN-II-ID-2052/2009), were finalized and the results were published in an article (sent at the end of 2012, published in early 2013).[3] It should be mentioned here that this paper was selected to illustrate the cover of the corresponding issue of the prestigious journal *Dalton Transactions*.[3] The imino organic ligands were also used to obtain new organobismuth(III) compounds (Scheme 1). The chlorides **11**, **12** și **13** were isolated as yellow crystalline powders, stable in air.



Scheme 1

New chiral halides of the type [2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}C_6H_4]PhSbCl (**15**) were isolated as stable compounds following reactions similar to that in Scheme 2. The compounds were characterized by elemental analysis, NMR and IR spectroscopy, mass spectrometry. For several organoantimony(III) and –bismuth(III) species the crystal and molecular structure was established by single-crystal X-ray diffraction.



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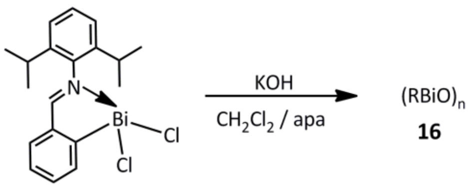
Scheme 2

Oxides and hydroxides/alkoxides, as well as ionic organometallic compounds (Sb, Bi)

Chiral oxides of the type $(RR'M)_2O$ and $(RMO)_2$ were prepared using organometallic halides described above. Thus, the oxide *ciclo*-[2-{(2',6'-$^{i}Pr_2C_6H_3$)N=CH}C_6H_4BiO]$_3$ (**16**) was obtained by reacting the chloride **12** with KOH, in a mixture of solvents, *i.e.* water / CH_2Cl_2 (Scheme 3). This oxide was isolated as a white, crystalline solid. All the oxides prepared were spectroscopically characterized.



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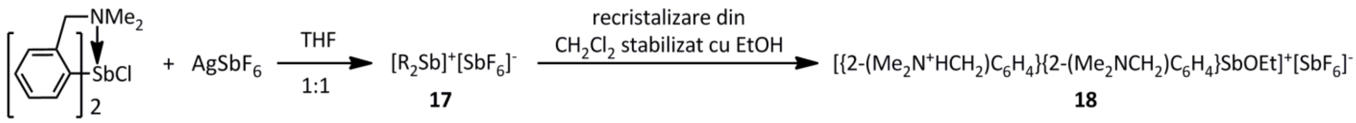
Scheme 3

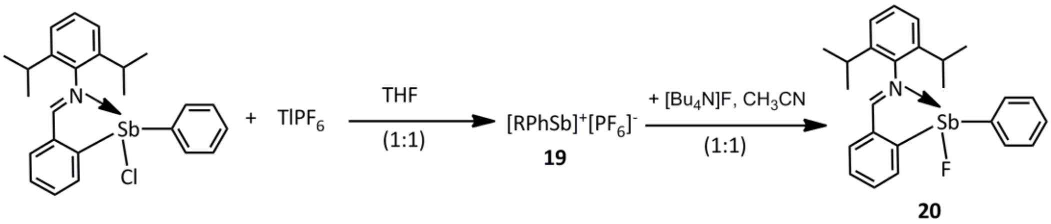
The synthesis of organometallic hydroxides and alkoxides appeared to be much more difficult, in most cases only oxides being obtained following elimination of water or ethers. The studies concerning the stabilization of such species are in progress as result of the serendipitous isolation of the ionic species [{2-($Me_2N^+HCH_2$)C_6H_4}{2-(Me_2NCH_2)C_6H_4}SbOEt]$^+$[SbF_6]$^-$ (**18**) (Scheme 4). The cation of this compound is chiral and the crystal contains a racemic mixture [(C_{Sb}) and (A_{Sb}) isomers] (Figure 1,a).



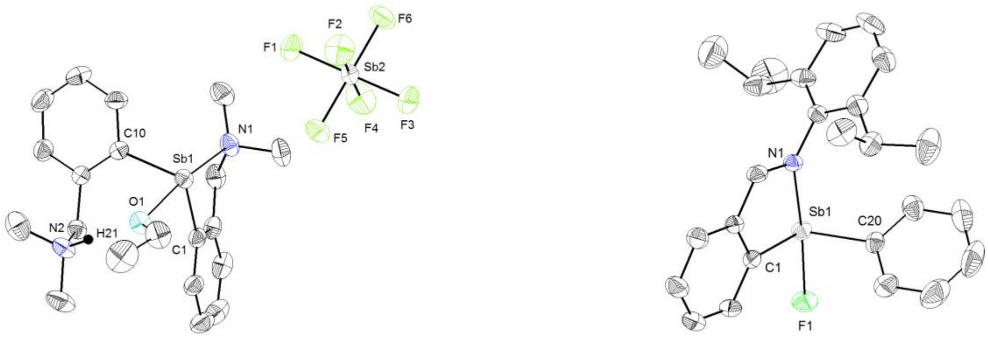
Scheme 4

Preliminary evaluations were performed to establish the ability of some organobismuth(III) and organoantimony(III) oxides to react with CO_2 or to catalyze reactions to obtain polycarbonates and/or cyclic organic carbonates from epoxides and CO_2.

The monochlorides [2-(Me_2NCH_2)C_6H_4]$_2$SbCl and **15** react with Ag[SbF_6] or Tl[PF_6] to give ionic species **17** (Scheme 4) and **19** (Scheme 5), with diorganoantimony(III) cations. Treatment of the ionic compound **19** with [Bu_4N]F·3H_2O gave the fluoride [2-{(2',6'-$Pr^{i}_2C_6H_3$)N=CH}C_6H_4]PhSbF (**20**) (Schema 5). The solution behaviour of the new ionic compounds **17** and **19** and of the fluoride **20** was investigated by multinuclear (^{1}H, ^{13}C si ^{19}F) NMR spectroscopy and the molecular structure of **20** was established by single-crystal X-ray diffraction (Figure 1,b). Preliminary results were presented at an international conference (C1 on the list of contributions to national and international conferences).



Scheme 5



(a) (b)

Figure 1. Structures of ionic compounds (a) (A_{Sb})-**18**, and (b) (C_{Sb})-**20**.

Within a collaboration with the research group of Prof. Ulrich Kortz (Jacobs University, Bremen, Germany) organoantimony(III) fragments – PhSb(III) and [2-(Me_2NCH_2)C_6H_4]Sb – were successfully incorporated in discrete heteropolytungstate anions, the results obtained being published in a joint paper.[4]

Due to difficulties concerning the preparation of new hypervalent R_2Bi-BiR_2 species by reduction of the organometallic halides obtained during this phase of the project, this target was postponed for future phases of the project.

Transition metal complexes based on organoantimony(III) ligands

Preliminary studies to obtain transition metal complexes (Ni, Pd) with chiral hypervalent compounds of the type $RSbPh_2$ were performed. Reactions between [2-(Ph_2NCH_2)C_6H_4]$SbPh_2$ and [2-{Mes(Me)NCH_2}C_6H_4]$SbPh_2$ (both compounds prepared within this phase of the project) and (cod)$PdCl_2$ (cod = 1,5-cyclooctadiene) were carried out in THF, at room temperature (Scheme 6). The work-up of the reaction mixtures did not yet produced pure complexes.

$$RSbPh_2 \xrightarrow{(cod)PdCl_2,\ THF} [(RSbPh_2)_2PdCl_2] \qquad \begin{array}{l} \mathbf{21}\text{: R = 2-(Ph}_2\text{NCH}_2\text{)C}_6\text{H}_4 \\ \mathbf{22}\text{: R = 2-[Mes(Me)NCH}_2\text{C}_6\text{H}_4 \end{array}$$

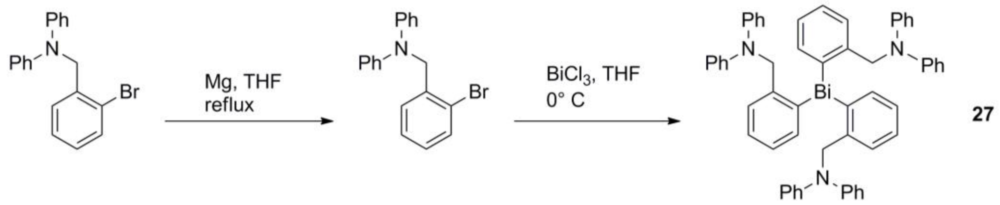
Scheme 6

Phase Jan.-Dec. 2013

Chiral organometallic compounds (Sb, Bi) with organic ligand bearing one or two pendant arms

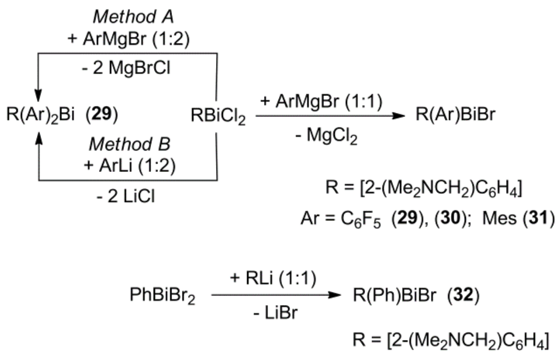
Several new organic ligands with one pendant arm, *e.g.* 2-(Ph_2NCH_2)C_6H_4Br or 2-[Mes(Me)NCH_2]C_6H_4Br, prepared during the previous phase, were used for the synthesis of chiral organoantimony(III) and organobismuth(III) species, *e.g.* [2-(Ph_2NCH_2)C_6H_4]$SbCl_2$ (**23**), [2-(Ph_2NCH_2)C_6H_4]$_2$SbCl (**25**) or [2-(Ph_2NCH_2)C_6H_4]$_3$Bi (**27**) (Scheme 7). Two new homoleptic triorganopnicogen(III) species, [2-($^iPr_2NCH_2$)C_6H_4]$_3$M [M = Sb (**28a**), Bi (**28b**)] were obtained by reacting [2-($^iPr_2NCH_2$)C_6H_4]MgBr (prepared *in situ* from [2-($^iPr_2NCH_2$)C_6H_4]Br (**1**) and Mg filings] with MCl_3. These compounds are very useful starting materials in redistribution reactions to produce new organometallic

halides. All these compounds were investigated by NMR spectroscopy and mass spectrometry, and the molecular structure of some of them was established single-crystal X-ray diffraction.



Schema 7

Studies on chiral organobismuth(III) containing C_6F_5 groups on the metal centre were continued. $[2\text{-}(Me_2NCH_2)C_6H_4](C_6F_5)_2Bi$ (**29**) was obtained by reacting $[2\text{-}(Me_2NCH_2)C_6H_4]BiCl_2$ and C_6F_5MgBr (method A) or C_6F_5Li (method B), in 1:2 molar ratio. Other chiral bromides $[2\text{-}(Me_2NCH_2)C_6H_4](Ar)BiBr$ [Ar = C_6F_5 (**30**), Mes (**31**)] and $[2\text{-}(Me_2NCH_2)C_6H_4](Ph)BiBr$ (**32**) (Scheme 8) were also obtained.

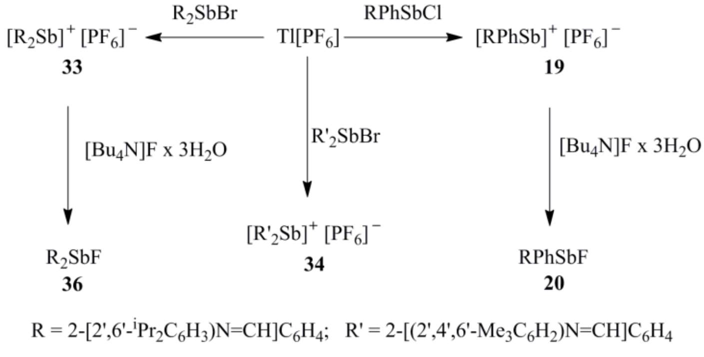


Schema 8

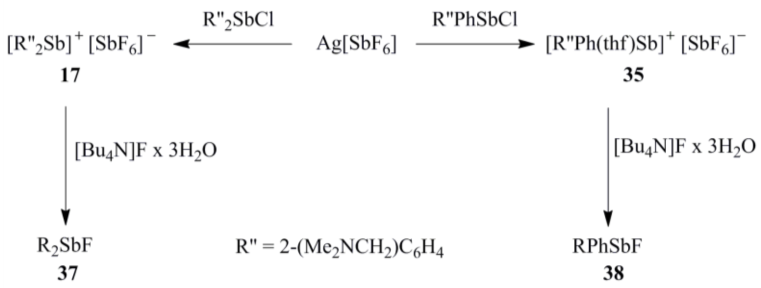
The compounds **31** and **32** are stable in air, while the derivatives **29** and **30**with C_6F_5 groups on bismuth decomposed in solution in few hours. All compounds were characterized in solution by NMR spectroscopy and their molecular structure was established single-crystal X-ray diffraction. In the crystal there were evidenced dimeric associations or 3D architectures based on Bi···halogen, H···halogen, H-π or π-π intermolecular interactions.

Organoantimony(III) ionic species and fluorides

The studies on the synthesis of diorganoantimony(III) cations and their use to prepare diorganoantimony(III) fluorides were continued and developed to get new chiral species stabilized using ligands with pendant arms, e.g. $2\text{-}[2',6'\text{-}{}^{i}Pr_2C_6H_3N{=}CH]C_6H_4$ and $2\text{-}[2',4',6'\text{-}Me_3C_6H_2N{=}CH]C_6H_4$. It was established a general, unique procedure for the preparation of diorganoantimony(III) fluorides, compounds which cannot be prepared using common methods of fluorination (Schemes 9 and 10).



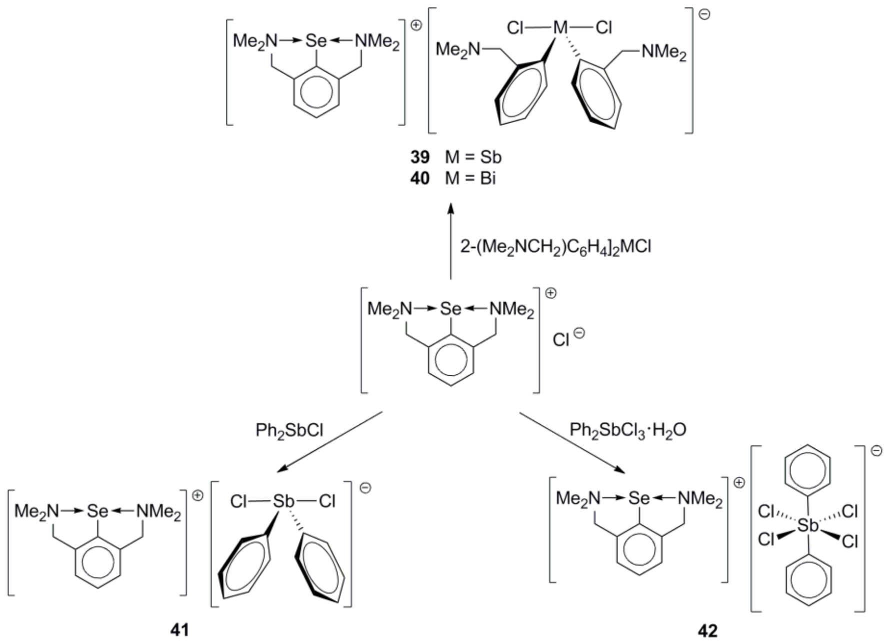
Scheme 9



Scheme 10

The solution behaviour of these new compounds was investigated by NMR spectroscopy at room temperature and for several compounds the molecular structure was established single-crystal X-ray diffraction.

Another strategy to obtain ionic organopnicogen species was based on the transfer of the chlorine atom from $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+Cl^-$ to the metal atom of organometallic chlorides of the type R'_2MCl_n (Scheme 11). The compounds were investigated in solution by multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{77}Se, 2D experiments). The ionic nature of these compounds containing diorganoantimonate anions was confirmed by conductometric studies and by the solid state structure determination by single-crystal X-ray diffraction for $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+[Ph_2SbCl_4]^-$ (**42**) (Figura 2). The results were published in an article which also includes theoretical calculations on these ionic species (sent in autumn of 2013, published in early 2014).[5]



Scheme 11

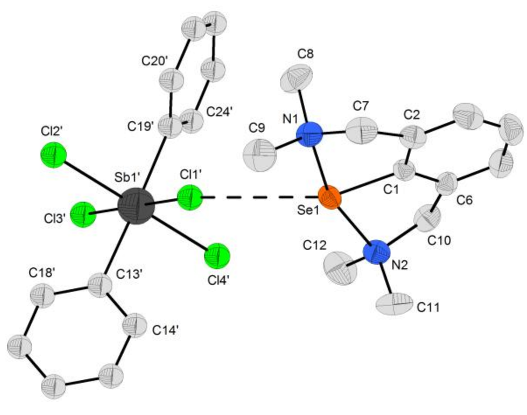
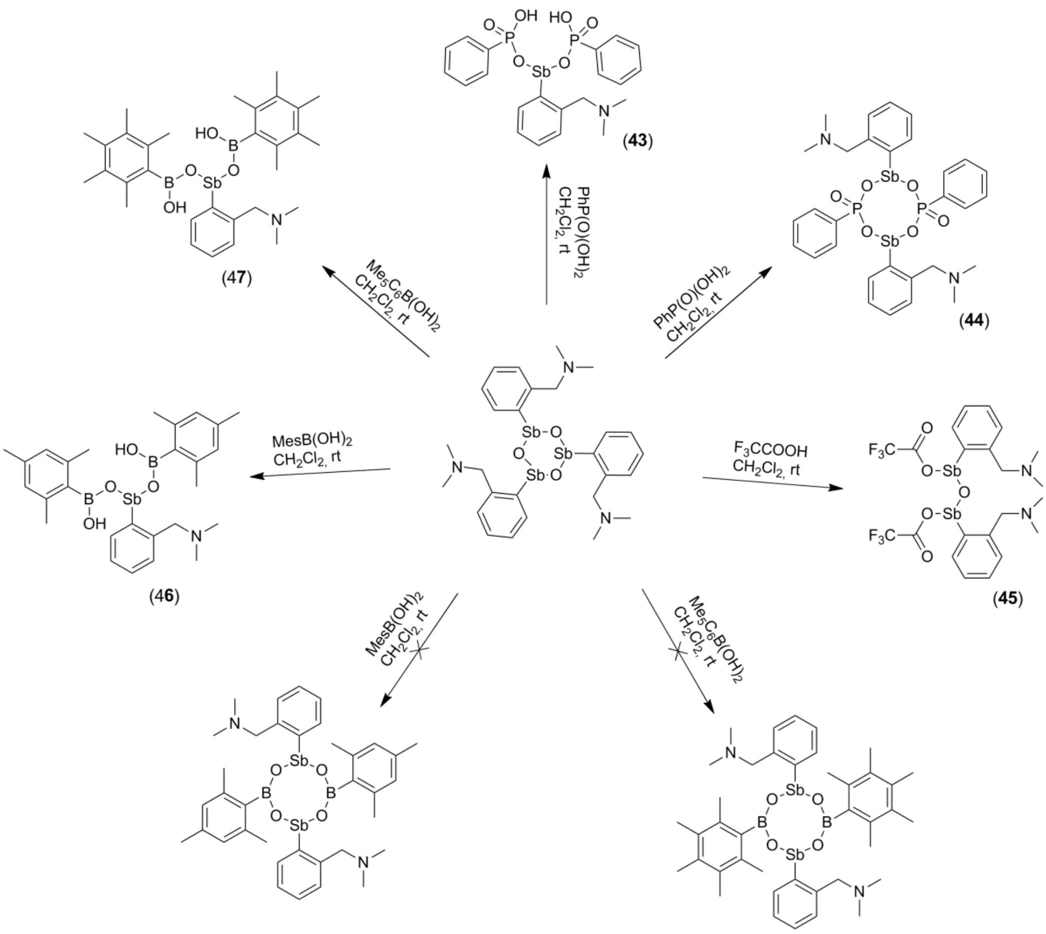


Figure 2. The structure of the ionic compound $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+[Ph_2SbCl_4]^-$ (**42**).

Organometallic (Sb, Bi) oxides and hydroxides/alkoxides

Studies were performed on the synthesis and characterization of new organoantimony(III) compounds containing the ligand 2-(Me_2NCH_2)C_6H_4, which might exhibit potential uses for the activation of small molecules. For this purpose the pnicogen/boron dinuclear species seem to be very promising since they have in the same molecule both Lewis acid and Lewis base centers. The oxide $(RSbO)_3$ was reacted with $PhP(O)(OH)_2$, $F_3CC(O)OH$, $MesB(OH)_2$ and $Me_5C_6B(OH)_2$ to produce new compounds (**43 - 47**) (Scheme 12), which were characterized through spectroscopic methods.



Scheme 12

The molecular structure of **45** was established by single-crystal X-ray diffraction on crystals grown by slow diffusion of petroleum ether into a chloroform solution of the compound (Figure 3).

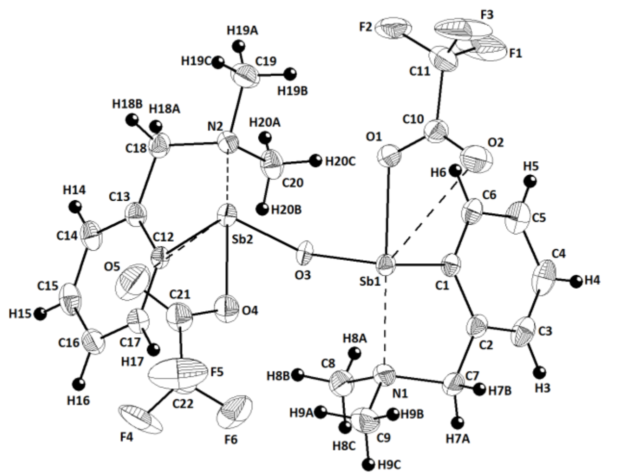


Figure 3. Structure of compound [{2-(Me_2NCH_2)C_6H_4}Sb{O(O)CCF_3}$_2$O (**45**).

Catalytic studies

The catalytic activity of some of the new chiral, hypervalent ionic organoantimony(III) compounds was investigated and studies on the efficiency on "one-pot" diastereoselective Mannich reactions were performed. This reaction is a useful way to build new C-C bonds. For the system of reagents used it was observed that the reaction is fast and efficient, with very good yields, depending on the reaction solvent. The *anti/syn* ratio in the reaction mixture was established by NMR spectroscopy.

It was established that the catalytic activity of the screened ionic species is higher than that of a neutral diorganoantimony(III) bromide or $SbCl_3$, in ethanol or acetonitrile.

Preliminary results were reported within a scientific conference on catalysis (C3 on the list of contributions to national and international conferences); the studies will be continued and finalized in a publication during the next phases of the project.

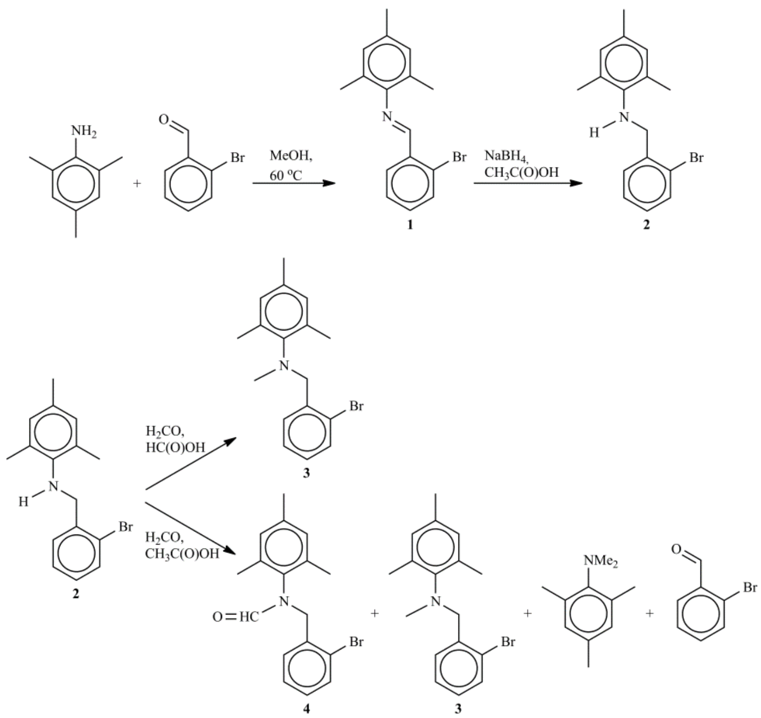
Transition metal complexes based on organoantimony(III) ligands

The studies on the synthesis and characterization of new palladium complexes with chiral, hypervalent organoantimony(III) ligands of the type $[2\text{-}(Me_2NCH_2)C_6H_4]PhSbCl$ and $[2\text{-}(Me_2NCH_2)C_6H_4]Mes_2Sb$ were continued. The stable species $[(Me_2NHCH_2)C_6H_5][\{2\text{-}(Me_2NCH_2)C_6H_4\}(Ph)(Cl)SbPdCl_3]$ (**49**) and *cis*-$[PdCl_2\{2\text{-}(Me_2NCH_2)C_6H_4\}Mes_2Sb]$ (**50**) were isolated and characterized in solution and solid state. Theoretical calculation at DFT level were carried out to get information on the nature of the coordinative bonds in these complexes. The results were published in an article (sent in autumn of 2013, published in early 2014).[6]

Phase Jan.-Dec. 2014

Chiral organometallic compounds (Sb, Bi) with organic ligand bearing one or two pendant arms

The studies concerning some of the new ligands with one pendant arm, including some of them which were developed during previous phases (Scheme 13), were finalized and the results are reported in an article accepted for publication.[7]



Scheme 13

The same applies for two new homoleptic triorganopnicogen(III) derivatives, $[2-(^iPr_2NCH_2)C_6H_4]_3M$ [M = Sb (**2**), Bi (**3**)], the synthesis of which is reported in an article accepted for publication, together with their full characterization in solution and solid state.[8]

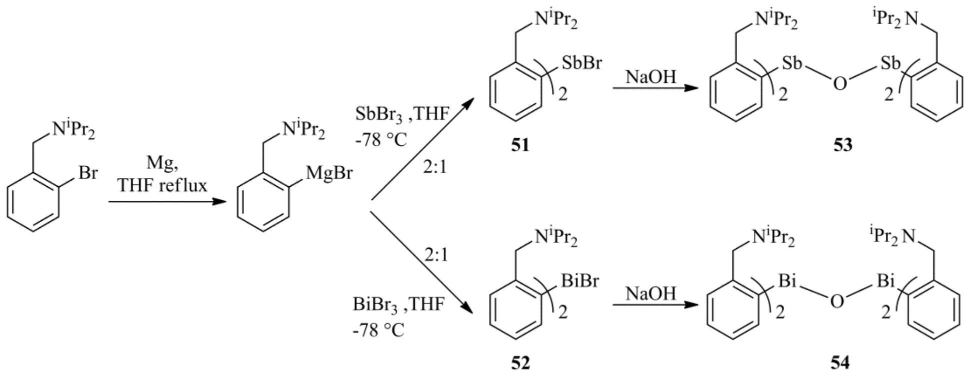
The solution behaviour of the cationic, diorganoantimony(III) species and of the corresponding fluorides prepared during the previous phases of the project was fully investigated by NMR spectroscopy, including experiments at variable temperature to reveal the dynamic nature of these compounds. The studies are finalized and the manuscript in under evaluation at the foreign partner (Prof. Michael Mehring, Technische Universitat Chemnitz) in collaboration with whom this work was developed. The manuscript will be submitted for publication during early April 2015.[9]

A manuscript reporting the results obtained in the studies on chiral, hypervalent diorganobismuth(III) compounds including those which contain a perfluorurated aromatic group attached to the metal centre is in the final stage of writing and intended to be submitted for publication on late April or May 2015.[10] The delay in publication with respect to the intention declared in the year report 2013 was due to the necessity to repeat some synthesis and variable NMR investigations of the title compounds.

Studies on the catalytic activity of compounds of the type $(R_2M)_2O$, $(RMO)_n$ (M = Sb, Bi)

Synthesis and characterization of organopnicogen oxides and alkoxides

Oxides of the type $(R_2M)_2O$ were prepared from the corresponding bromides $[2-(^iPr_2NCH_2)C_6H_4]_2MBr$ [M = Sb (**51**), Bi (**52**)]. The bromides used as starting materials and the oxides $[\{2-(^iPr_2NCH_2)C_6H_4\}_2M]_2O$ [M = Sb (**53**), Bi (**54**)] (Schema 14) were fully characterized by NMR spectroscopy, mass spectroscopy and single-crystal X-ray diffraction (for the bromides – Figure 4).



Scheme 14

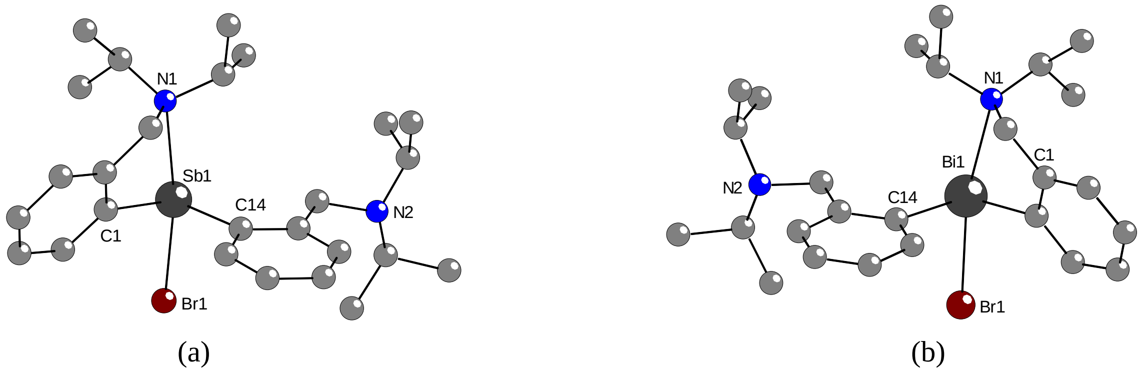
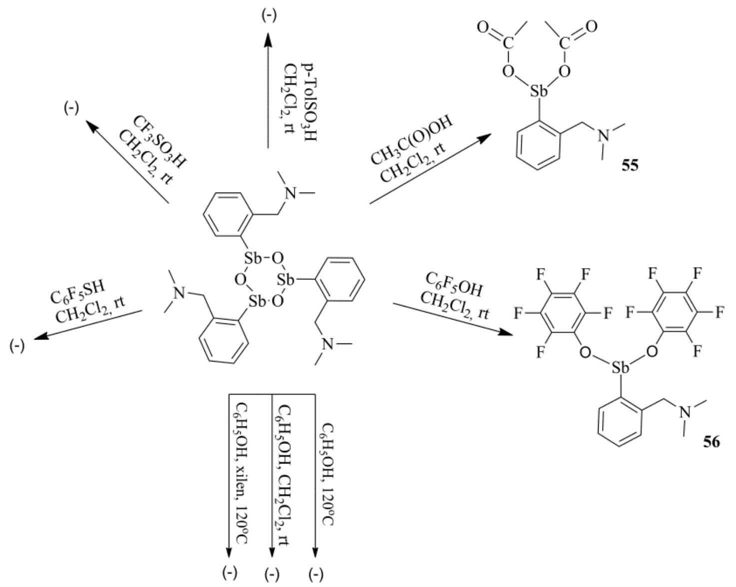


Figure 4. Molecular structure of (a) $[2-(^iPr_2NCH_2)C_6H_4]_2SbBr$ (**51**), and (b) $[2-(^iPr_2NCH_2)C_6H_4]_2BiBr$ (**52**).

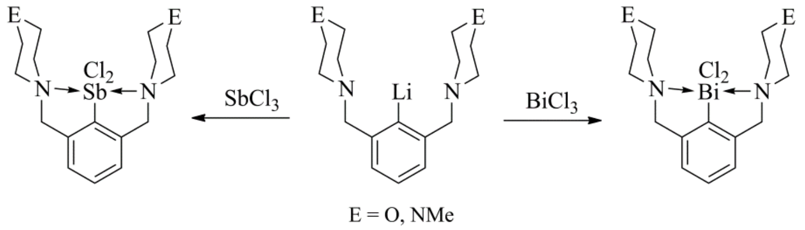
Studies were carried out on the reactivity of the cyclic oxide $[\{2-(Me_2NCH_2)C_6H_4\}SbO]_3$ towards acetic acid, sulfonic acids, phenols and thiophenols (Scheme 15), in order to obtain new organoantimony(III) compounds with

potential to activate small molecules. The reactions with sulfonic acids, phenol and thiophenol C_6F_5SH failed to produce the desired compounds, the reactions with acetic acid and C_6F_5OH gave the new species **55** and **56**.

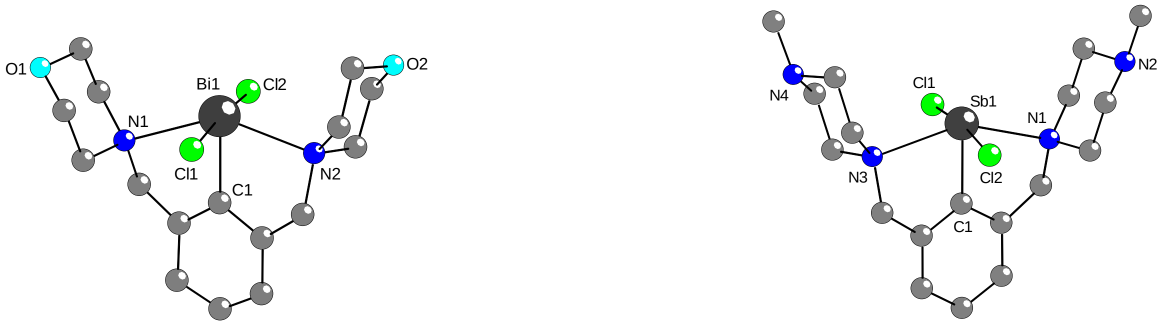


Scheme 15

Studies were performed on the synthesis of organometallic oxides, alkoxides and aryloxides containing an aromatic ligand with two pendant arms. The dichlorides [2,6-{$O(CH_2CH_2)_2NCH_2$}$_2C_6H_3$]MCl_2 [M = Sb (**57**), Bi (**58**)] and [2,6-{$MeN(CH_2CH_2)_2NCH_2$}$_2C_6H_3$]MCl_2 [M = Sb (**59**), Bi (**60**)] (Scheme 16) were prepared and fully characterized from spectroscopic point of view. The molecular structure of the dichlorides **58** and **59** was established by single-crystal X-ray diffraction (Figure 5).



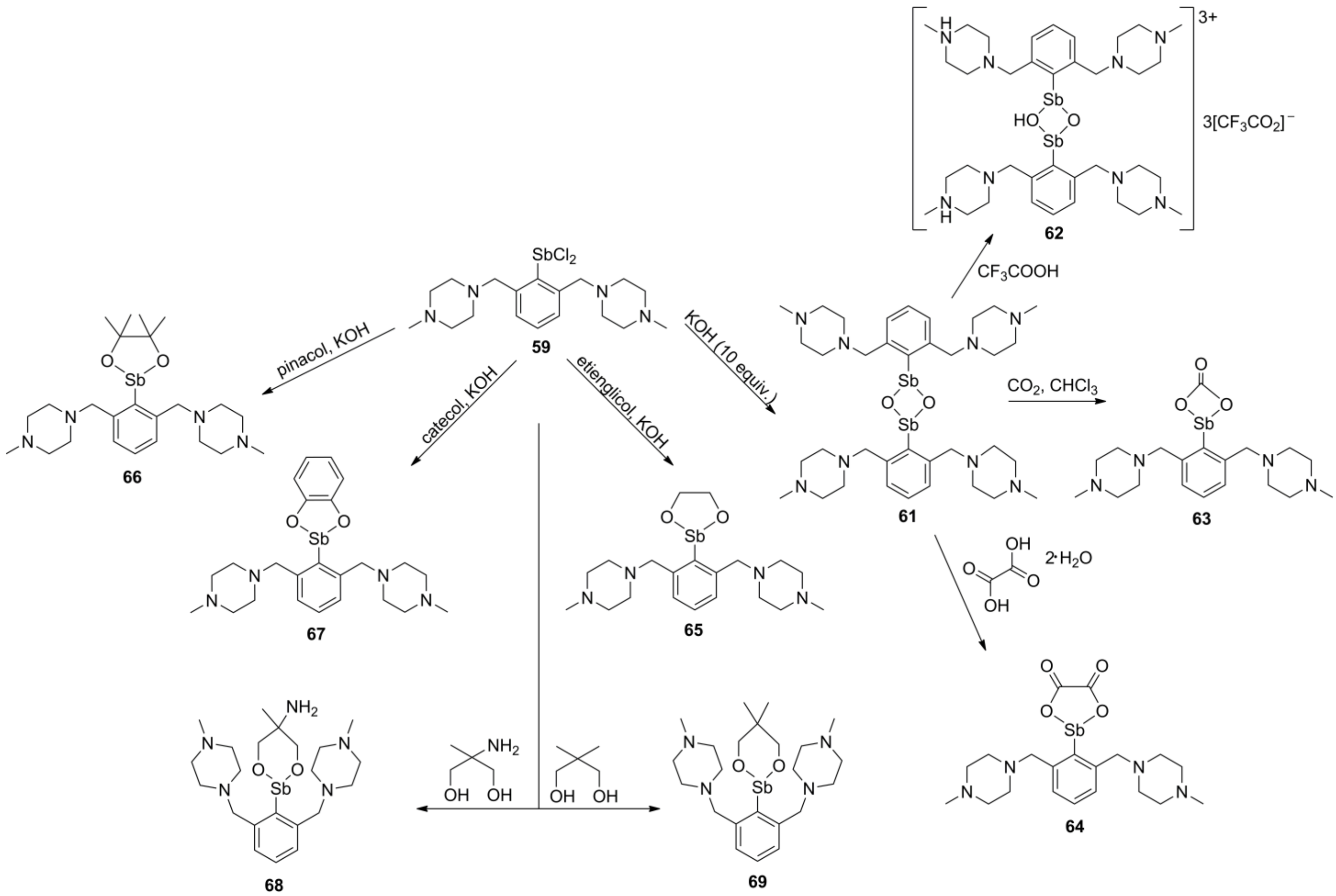
Scheme 16



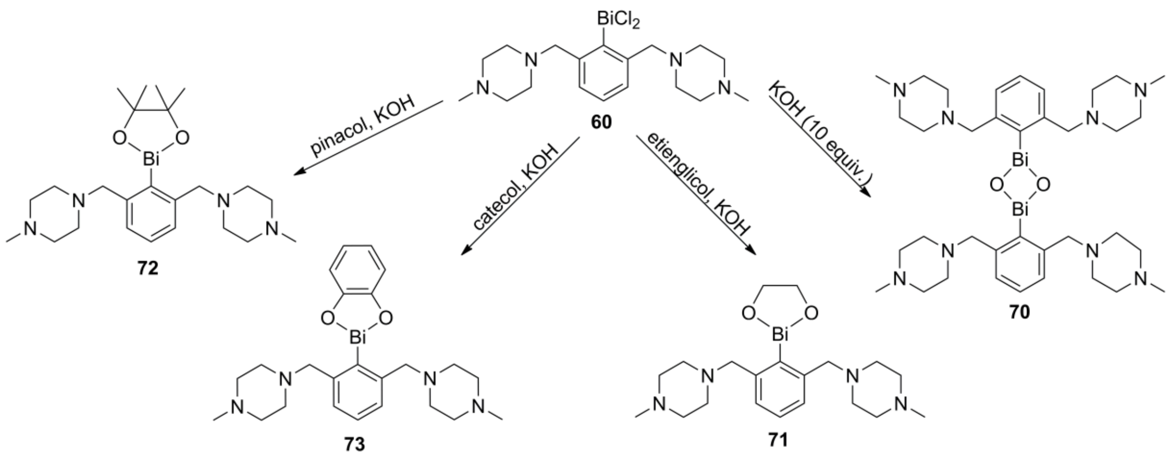
(a) (b)

Figure 5. Molecular structure of (a) [2,6-{$O(CH_2CH_2)_2NCH_2$}$_2C_6H_3$]$BiCl_2$ (**58**), and (b) [2,6-{$MeN(CH_2CH_2)_2NCH_2$}$_2C_6H_3$]$SbCl_2$ (**59**).

The dichlorides **59** and **60** were used as starting materials for the preparation of oxides of the type $(RMO)_2$ as well as the synthesis of chelate alkoxides/aryloxides, potential candidates for CO_2 caption (Schemes 17 and 18). The oxides **61** și **70** were isolated as white, crystalline solids. They were investigated spectroscopically (multinuclear NMR, MS) and their molecular structure was established by single-crystal X-ray diffraction (Figure 6).



Scheme 17



Scheme 18

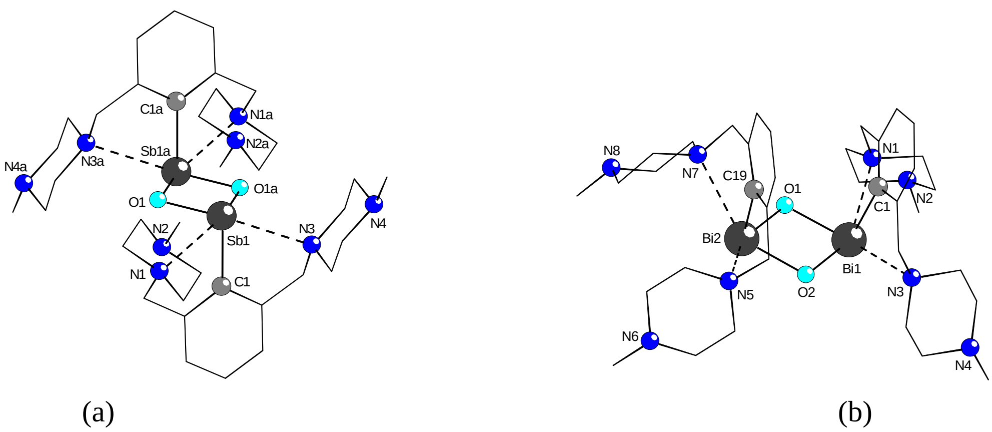


Figure 6. Molecular structure of (a) *cyclo*-[2,6-$\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]_2Sb_2O_2$ (**61**), and (b) *cyclo*-[2,6-$\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]_2Bi_2O_2$ (**70**).

The compounds were isolated as white crystalline solids, stable in air. They were characterized using complex NMR studies, in addition to IR spectroscopy and mass spectrometry. For compounds $[\{2,6\text{-}(MeN\{CH_2CH_2\}_2NCH_2)_2C_6H_3\}_2Sb_2O_2(H)_3](O_2CCF_3)_3$ (**62**), $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]M(OCH_2)_2$ [M = Sb (**65**), Bi (**71**)], $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Sb(OCMe_2)_2$ (**66**), $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]M(O_2\text{-}1,2\text{-}C_6H_4)$ [M = Sb (**67**), Bi (**73**)] and $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Sb[O(O)CC(O)O]$ (**64**) the molecular structure was established by single-crystal X-ray diffraction (Figure 7). These results are reported in a manuscript submitted for publication, being now under evaluation (*the manuscript was submitted initially to Chemical Science and transferred to Dalton Transactions as recommended by the editor*).[11]

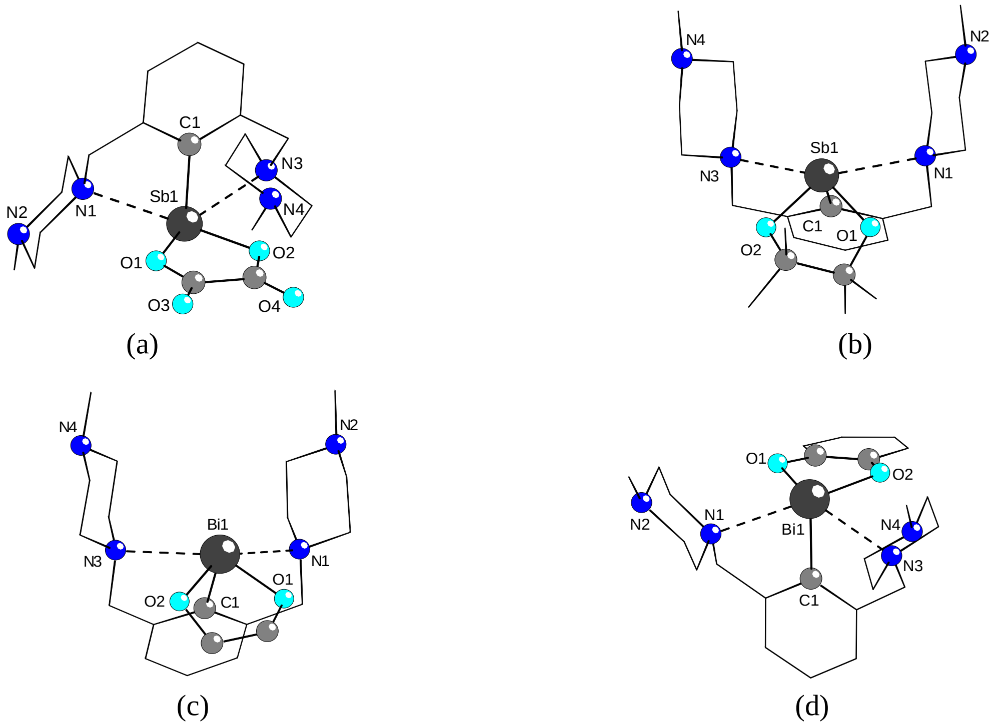
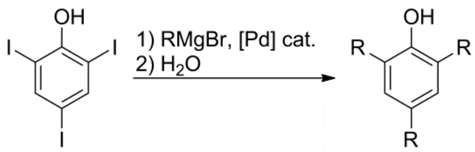


Figure 7. Molecular structure of (a) $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Sb[O(O)CC(O)O]$ (**64**), (b) $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Sb(OCMe_2)_2$ (**66**), (c) $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Bi(OCH_2)_2$ (**71**), and (d) $[2,6\text{-}\{MeN(CH_2CH_2)_2NCH_2\}_2C_6H_3]Bi(O_2\text{-}1,2\text{-}C_6H_4)$ (**73**).

Two phenols with terphenyl backbone, $2,4,6\text{-}R_3C_6H_2OH$ [R = $2,4,6\text{-}Me_3C_6H_2$ (**74**), Me_5C_6 (**75**)], were prepared using Kumada coupling reactions between $2,4,6\text{-}I_3C_6H_2OH$ and the corresponding Grignard reagent (Scheme 19). These phenols will be used in the synthesis of organopnicogen derivatives. Both compounds were characterized using multinuclear NMR spectroscopy and HRMS, and their molecular structure was established by single-crystal X-ray diffraction. The results are reported in a published paper.[12]

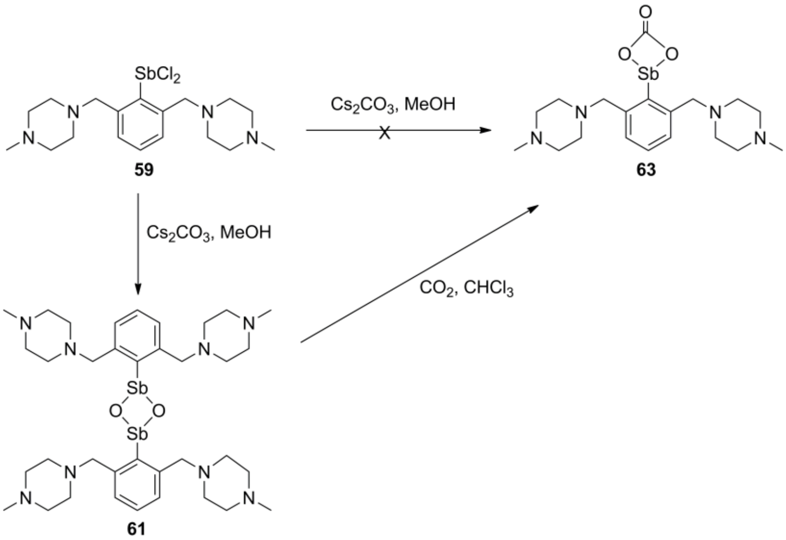


Scheme 19

Screening of the capacity to react with CO_2 and preliminary studies on the catalytic activity

Preliminary studies were performed on the capacity of some organobismuth(III) and -antimony(III) oxides to react with CO_2 and to catalyze reactions between epoxides and CO_2 to give organic polycarbonates and/or cyclic carbonates.

The carbonate **63** was obtained by passing gaseous CO_2 through a solution of the oxide **61** in chloroform. Attempts to obtain **63** from the dichloride **59** and caesium carbonate failed, only the oxide **61** being isolated (Scheme 21). No CO_2 absorption by the alkxide **65** in chloroform was observed.



Scheme 20

The carbonate **63** was also screened as catalyst for the reaction of epoxides and CO_2. To develop this type of studies a specific infrastructure is required to allow experiments at high pressure and this will be a priority for the next phase of the project.

The organobismuth(III) alkoxides **71** – **73** were also screened as CO_2 activators and the reactions were monitorized by NMR spectroscopy.

Studies on the catalytic activity of hypervalent compounds of the type $[R_2M]^+X^-$

The studies on the catalytic activity of some new cationic, hypervalent organoantimony(III) species in the case of the "one-pot" Mannich reactions were continued. The nfluence of the solvent was investigated. The compounds screened proved to be useful to catalyze such reaction to build new C-C bonds. The catalytic activity of our compounds was compared with that of a compound reported in the literature, $C_6H_{11}N(C_6H_4CH_2)_2SbOSO_2CF_3$.[13] Evidences were obtained with respect to the stability of an organoantimony catalyst and to the possibility for repeat use without lost of the catalytic activity in the Mannich system tested.

References

1. *Hypervalent organoantimony and -bismuth compounds with pendant arm ligands*, C. I. Raţ, C. Silvestru, H. J. Breunig, *Coord. Chem. Rev.*, **2013**, *257*, 818-879; DOI: 10.1016/j.ccr.2012.07.026.

2. *New chiral organoantimony(III) compounds containing intramolecular N→Sb interactions – solution behaviour and solid state structures*, D. Copolovici, V. R. Bojan, C. I. Raţ, A. Silvestru, H. J. Breunig, C. Silvestru, *Dalton Trans.*, **2010**, *39*, 6410-6418; DOI: 10.1039/c003318a.

3. *Organoantimony(III) compounds containing (imino)aryl ligands of the type 2-(RN=CH)C_6H_4 (R = 2′,4′,6′-$Me_3C_6H_2$, 2′,6′-$^iPr_2C_6H_3$): bromides and chalcogenides*, A. M. Preda, C. I. Raţ, C. Silvestru, H. J. Breunig, H. Lang, T. Rüffer, M. Mehring, *Dalton Trans.*, **2013**, *42*, 1144-1158; DOI: 10.1039/C2DT32494F.

4. *Synthesis and characterization of organoantimony(III)-containing heteropolytungstates*, M. Barsukova-Stuckart, L. F. Piedra-Garza, B. Gautam, G. Alfaro-Espinoza, N. V. Izarova, A. Banerjee, B. Bassil, M. Ullrich, H. J. Breunig, C. Silvestru, Ulrich Kortz, *Inorg. Chem.*, **2012**, *51*, 12015-12022; DOI: 10.1021/ic301892s.

5. *Organoselenium(II) halides containing the pincer 2,6-$(Me_2NCH_2)_2C_6H_3$ ligand – an experimental and theoretical investigation*, A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis, C. Silvestru, *Dalton Trans.*, **2014**, *43*, 2221-2233; DOI: 10.1039/C3DT52886C

6. *Palladium(II) complexes with chiral organoantimony(III) ligands. Solution behavior and solid state structures*, D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raț, C. Silvestru, *RSC Advances*, **2014**, *4*, 26569-26576; DOI: 10.1039/c4ra03482a

7. *Synthesis and characterization of 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br and 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br – Precursors for novel one pendant arm ligands*, G. Strîmb, C. I. Raț, C. Silvestru, *Rev. Roum. Chim.*, **2015**, *accepted* (Nr. omagial Valer FARCASAN).

8. *Homoleptic organometallic compounds of heavy pnicogens. Crystal and molecular structure of [2-(^{i}Pr$_2$NCH$_2$)C$_6$H$_4$]$_3$M (M = Sb, Bi),* I. Chircă, A. Soran, A. Silvestru, C. Silvestru, *Rev. Roum. Chim.*, **2015**, *accepted* (Nr. omagial Valer FARCASAN).

9. *Hypervalent diorganoantimony(III) fluorides via diorganoantimony(III) cations – a general method of synthesis*, A. M. Preda, C. I. Raţ, C. Silvestru, H. Lang, T. Rüffer, M. Mehring, *manuscript on final stage of preparation; to be submitted on early April 2015*.

10. *Hypervalent triorganobismuthine, RBi(C$_6$F$_5$)$_2$ and racemic Bi-chiral diorganobismuth(III) bromides R(C$_6$F$_5$)BiBr, R(Mes)BiBr, R(Ph)BiBr with the pendant arm ligand [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$]*, M. Nema, C. Silvestru, A. Soran, H. J. Breunig, *manuscript on final stage of preparation; to be submitted on May 2015*.

11. *A general route to monoorganopnicogen(III) (M = Sb, Bi) compounds with a pincer (N,C,N) group and oxo ligands*, G. Strîmb, A. Pöllnitz, C. I. Raţ, C. Silvestru, *manuscript under evaluation at Dalton Transactions*.

12. *Synthesis and structural characterization of substituted phenols with m-terphenyl backbone, 2,4,6-R$_3$C$_6$H$_2$OH (R = 2,4,6-Me$_3$C$_6$H$_2$, Me$_5$C$_6$),* A. B. Șolea, M. Olaru, C. Silvestru, C. I. Raț, *Z. Naturforsch., B: Chem. Sci.*, **2015**, *70*, 77-81; DOI: 10.1515/znb-2014-0180

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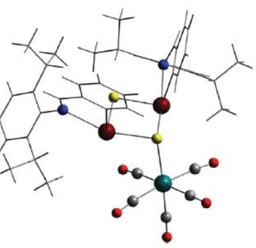
1. **Hypervalent organoantimony and -bismuth compounds with pendant arm ligands**,
C. I. Raţ, C. Silvestru and H. J. Breunig,
Coord. Chem. Rev., **2013**, *257*, 818-879.
DOI: 10.1016/j.ccr.2012.07.026

A B S T R A C T

Recent developments in chemistry of hypervalent organoantimony and -bismuth complexes with bidentate (*C,E*)- and tridentate (*E,C,E*)- and (*C,E,C*)-ligands are reviewed. The ligands are bonded to the antimony or bismuth atoms through carbon atoms and through intramolecular coordination with dative bonds from nitrogen, oxygen or sulfur atoms. Syntheses, structures including chirality aspects, reactions, fluxional behavior, biological aspects and applications in the field of catalysis and organic syntheses are considered in this review.

3. **Organoantimony(III) compounds containing (imino)aryl ligands of the type 2-(RN=CH)C_6H_4 (R = 2′,4′,6′-$Me_3C_6H_2$, 2′,6′-$^iPr_2C_6H_3$): bromides and chalcogenides**,
A. M. Preda, C. I. Raţ, C. Silvestru, H. J. Breunig, H. Lang, T. Rüffer and M. Mehring,
Dalton Trans., **2013**, *42*, 1144-1158.
DOI: 10.1039/C2DT32494F

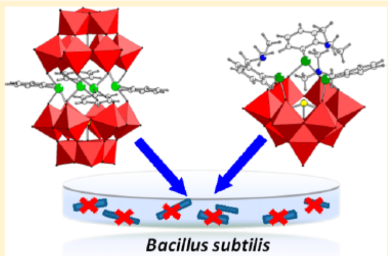


ABSTRACT

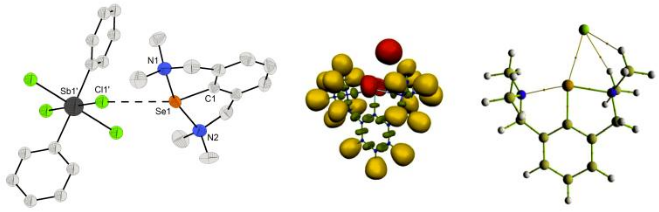
The reaction of 2-(RN═CH)C_6H_4MgBr [R = 2′,4′,6′-$Me_3C_6H_2$ (R^1), 2′,6′-$^iPr_2C_6H_3$ (R^2)] [prepared from 2-(R^1N═CH)C_6H_4Br (**1**) or 2-(R^2N═CH)C_6H_4Br (**2**) and Mg] with $SbCl_3$ in a 2 : 1 and 1 : 1 molar ratio followed by treatment with an aqueous KBr solution gave [2-(R^1N═CH)C_6H_4]$_2$SbBr (**3**) and [2-(R^2N═CH)-C_6H_4]$_2$SbBr (**4**) as well as [2-(R^1N═CH)C_6H_4]$SbBr_2$ (**6**) and [2-(R^2N═CH)C_6H_4]$SbBr_2$ (**7**). Treatment of **4** with $Na_2S{\cdot}9H_2O$ provided the dinuclear [{2-(R^2N═CH)C_6H_4}$_2$Sb]$_2$S (**5**). Heterocyclic species, *i.e.* the oxide *cyclo*-[{2-(R^2N═CH)C_6H_4}SbO]$_3$ (**8**) and the sulfides *cyclo*-[{2-(R^1N═CH)C_6H_4}SbS]$_2$ (**9**) and *cyclo*-[{2-(R^2N═CH)C_6H_4}SbS]$_2$ (**10**), were obtained by reacting dibromides **6** and **7** with KOH and $Na_2S{\cdot}9H_2O$, respectively, in a water–toluene solvent mixture. The sulfide **10** reacted with [W(CO)$_5$(thf)] to yield the heterometallic complex *cyclo*-[{2-(R^2N═CH)C_6H_4}SbS]$_2$[W(CO)$_5$] (**11**). The compounds were characterised by multinuclear NMR spectroscopy in solution, mass spectrometry and IR spectroscopy in the solid state. The molecular structures of **4**, **5**, **6**·$CHCl_3$, **7**, **9**·CH_2Cl_2, **10** and **11**·0.25CH_3OH were established by single-crystal X-ray diffraction. Theoretical calculations using DFT methods were carried out on bromide **7** and the geometrical isomers of its dimer association as well as the geometrical isomers of sulfide **10** and its monomer.

4. **Synthesis and characterization of organoantimony(III)-containing heteropolytungstates**,
M. Barsukova-Stuckart, L. F. Piedra-Garza, B. Gautam, G. Alfaro-Espinoza, N. V. Izarova, A. Banerjee, B. Bassil, M. Ullrich, H. J. Breunig, C. Silvestru and Ulrich Kortz,
Inorg. Chem., **2012**, *51*, 12015-12022.
DOI: 10.1021/ic301892s

ABSTRACT: Three discrete organoantimony(III)-containing heteropolytungstates [$(PhSb^{III})_4(A$-α-$Ge^{IV}W_9O_{34})_2]^{12-}$ (**1**), [$(PhSb^{III})_4(A$-α-$P^VW_9O_{34})_2]^{10-}$ (**2**), and [{2-$(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B$-$\alpha$-$As^{III}W_9O_{33})]^{3-}$ (**3**) have been synthesized in one-pot reactions in aqueous medium using the appropriate lacunary heteropolyanion precursor and organoantimony(III) source. Polyanions **1**−**3** were isolated as hydrated salts, $(NH_4)_{12}[(PhSb^{III})_4(A$-$\alpha$-$Ge^{IV}W_9O_{34})_2]{\cdot}20H_2O$ (**1a**), $Rb_9Na[(PhSb^{III})_4(A$-α-$P^VW_9O_{34})_2]{\cdot}20H_2O$ (**2a**), and $Rb_3[\{2$-$(Me_2NCH_2C_6H_4)Sb^{III}\}_3(B$-$\alpha$-$As^{III}W_9O_{33})]{\cdot}7H_2O$ (**3a**). The compounds **1a**−**3a** were fully characterized in the solid state using infrared (IR) spectroscopy, single-crystal XRD, and thermogravimetric and elemental analyses. The stability of **1**−**3** in aqueous solution was confirmed by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, and ^{183}W) spectroscopy. Preliminary studies on the biological activity of **1**−**3** showed that all three compounds might act as potent antimicrobial agents.



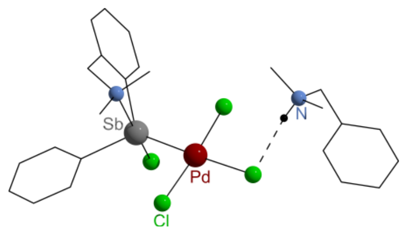
5. **Organoselenium(II) halides containing the pincer 2,6-$(Me_2NCH_2)_2C_6H_3$ Ligand – an experimental and theoretical investigation**,
A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis and C. Silvestru,
Dalton Trans., **2014**, *43*, 2221-2233.
DOI: 10.1039/C3DT52886C



ABSTRACT

New organoselenium(II) halides of the type $[RSe]^+X^-$ [R = 2,6-$(Me_2NCH_2)_2C_6H_3$; X = Cl (**2**), Br (**3**), I (**4**)] were prepared by cleavage of the Se–Se bond in R_2Se_2 (**1**) with SO_2Cl_2 followed by halogen exchange when organoselenium chloride was treated with NaBr or KI. The reaction between **2** and R'_2MCl_n resulted in new ionic $[RSe]^+[R'_2MCl_{n+1}]^-$ [R' = 2-$(Me_2NCH_2)C_6H_4$, n = 1, M = Sb (**5**), Bi (**6**); R' = Ph, M = Sb, n = 1 (**7**) or n = 3 (**8**)] species. All new compounds were investigated in solution by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{77}Se, 2D experiments) and mass spectrometry. The ionic nature of **2** and the antimonates species was confirmed by conductivity studies. The molecular structures of $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+Cl^-\cdot nH_2O$ (**2**·H_2O and **2**·$2H_2O$) and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}Se]^+[Ph_2SbCl_4]^-$ (**8**), respectively, were established by single-crystal X-ray diffraction, pointing out that the ionic nature of these compounds is also preserved in the solid state, with both nitrogen atoms strongly *trans* coordinated to the selenium atom of the cation. Theoretical calculations carried out at the DFT level were exploited to investigate the nature of the bonding in compounds **2–4** and the free cation $[RSe]^+$ (**2a**). A topological analysis based on the theory of Atoms-In-Molecules (AIM) and Electron Localization Function (ELF) jointly to a Natural Bond Orbital (NBO) approach was used to shed light on the effect of the nature of the halogen species X on the bonding within the 3c-4e N–Se–N moiety.

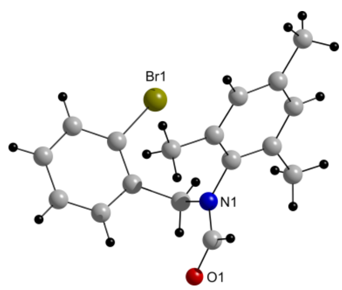
6. **Palladium(II) complexes with chiral organoantimony(III) ligands. Solution behavior and solid state structures**,
D. Copolovici, F. Isaia, H. J. Breunig, C. I. Raț and C. Silvestru,
RSC Advances, **2014**, *4*, 26569-26576.
DOI: 10.1039/c4ra03482a



ABSTRACT

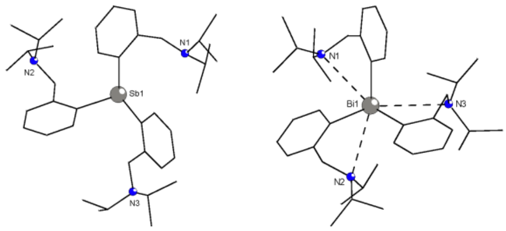
The chiral compound (2-$Me_2NCH_2C_6H_4$)PhSbCl (**1**) was obtained from (2-$Me_2NCH_2C_6H_4$)Li and $PhSbCl_2$ in 1 : 1 molar ratio, while (2-$Me_2NCH_2C_6H_4$)Mes_2Sb (**2**) was prepared from (2-$Me_2NCH_2C_6H_4$)$SbCl_2$ and MesMgBr in 1 : 2 molar ratio. The compounds **1** and **2** were used to obtain the Pd(II)/stibine complexes: $[Me_2NHCH_2C_6H_5]^+[PdCl_3\{SbCl(Ph)(C_6H_4CH_2NMe_2\text{-}2)\text{-}Sb\}]^-$ (**3**) and $[PdCl_2\{SbMes_2(C_6H_4CH_2NMe_2\text{-}2)\text{-}N,Sb\}]$ (**4**). All the compounds were characterized by multinuclear NMR spectroscopy in solution, elemental analysis, mass spectrometry and single-crystal X-ray diffraction studies. In compounds **1–3** the coordination geometry around the antimony atom is pseudo-trigonal bipyramidal, while in compound **4** a tetrahedral geometry around the antimony atom is observed. Theoretical calculations at the DFT level on compounds **1–4** were used in order to gain insight into the nature of the coordinative bonds.

7. **Synthesis and characterization of 2-[Mes(Me)NCH_2]C_6H_4Br and 2-[Mes{(O)CH}NCH_2]C_6H_4Br – Precursors for novel one pendant arm ligands,**
G. Strîmb, C. I. Raț and C. Silvestru,
Rev. Roum. Chim., **2015**, *accepted*. (Nr. omagial Valer FARCASAN).



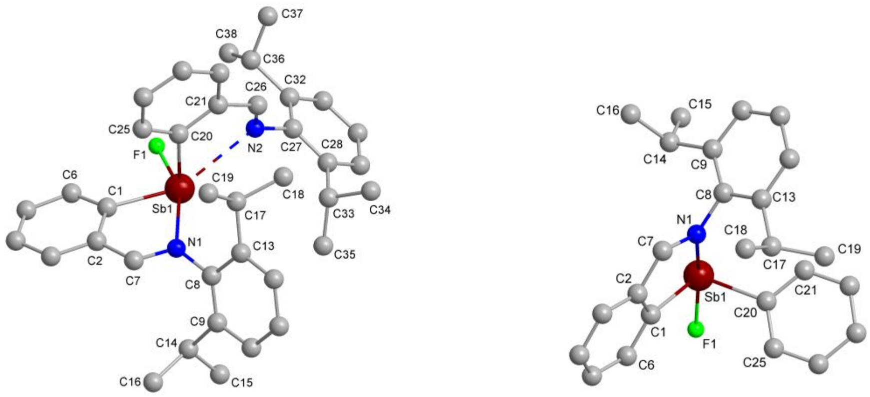
ABSTRACT: A new secondary amine 2-(MesNHCH$_2$)C$_6$H$_4$Br (**2**) was synthesized starting from imine 2-(MesN=CH)C$_6$H$_4$Br (**1**) and NaBH$_4$. Reaction of **2** with paraformaldehyde and HC(O)OH gave almost quantitatively 2-[Mes(Me)NCH$_2$]C$_6$H$_4$Br (**3**), while treatment of **2** with paraformaldehyde and CH$_3$C(O)OH resulted in **3** as a major product besides a minor amount of the unexpected 2-[Mes{(O)CH}NCH$_2$]C$_6$H$_4$Br (**4**) compound. The compounds were characterized by multinuclear NMR and IR spectroscopy, mass spectrometry and the molecular structure of **4** was established by single-crystal X-ray diffraction.

8. **Homoleptic organometallic compounds of heavy pnicogens. Crystal and molecular structure of [2-(^{i}Pr$_2$NCH$_2$)C$_6$H$_4$]$_3$M (M = Sb, Bi),**
I. Chircă, A. Soran, A. Silvestru and C. Silvestru,
Rev. Roum. Chim., **2015**, *accepted*. (Nr. omagial Valer FARCASAN)



ABSTRACT: Two new homoleptic triorganopnicogen(III) species, [2-(^{i}Pr$_2$NCH$_2$)C$_6$H$_4$]$_3$M [M = Sb (**2**), Bi (**3**)] were obtained by reacting [2-(^{i}Pr$_2$NCH$_2$)C$_6$H$_4$]MgBr (prepared *in situ* from [2-(^{i}Pr$_2$NCH$_2$)C$_6$H$_4$]Br (**1**) and Mg filings] with MCl$_3$. The compounds were characterized by multinuclear NMR solution studies and the crystal and molecular structure of **2** and **3** was established by single-crystal X-ray diffraction. The NMR data are consistent with one type of organic group attached to the metal atom in **2** and **3**. The main difference between the molecules of the organometallic species is observed in the solid state. While for the antimony(III) compound all pendant arms are twisted to push the nitrogen atoms far from the metal centre, in the bismuth(III) derivative weak intramolecular N→Bi interactions are established for all three nitrogen atoms, thus increasing the coordination number from three to six in a distorted octahedral (*C*,*N*)$_3$Bi core.

9. **Hypervalent diorganoantimony(III) fluorides via diorganoantimony(III) cations – a general method of synthesis**,
A. M. Preda, C. I. Raţ, C. Silvestru, H. Lang, T. Rüffer and M. Mehring, *manuscript on final stage of preparation; to be submitted on early April 2015.*

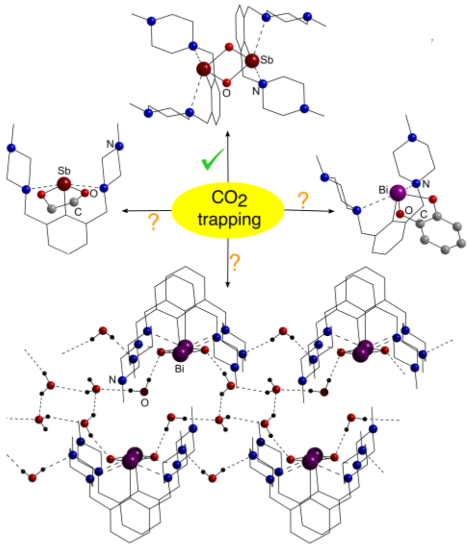


ABSTRACT: The novel diorganoantimony(III) fluorides containing ligands with pendant arms, R$_2$SbF (**5**), (R)PhSbF (**6**) [R = 2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$], R″$_2$SbF (**7**) and (R″)PhSbF (**8**) [R″ = 2-(Me$_2$NCH$_2$)C$_6$H$_4$], were prepared *via* the ionic derivatives [R$_2$Sb]$^+$[PF$_6$]$^-$ (**1**), [(R)PhSb]$^+$[PF$_6$]$^-$ (**2**), [R″$_2$Sb]$^+$[SbF$_6$]$^-$ (**4**) and [(R″)PhSb]$^+$[SbF$_6$]$^-$ (obtained *in situ*) by treatment with [Bu$_4$N]F·3H$_2$O. The ionic species used as starting materials as well as [R′$_2$Sb]$^+$[PF$_6$]$^-$ (**3**) [R′ = 2-(2′,4′,6′-Me$_3$C$_6$H$_2$N=CH)C$_6$H$_4$] were obtained from the corresponding bromides or chlorides and Tl[PF$_6$] or Ag[SbF$_6$]. The compounds were investigated by multinuclear NMR spectroscopy in solution, MS and IR spectroscopy in the solid state. The molecular structures of the ionic species **1**·2CH$_2$Cl$_2$ and **3**·2CHCl$_3$ as well as the fluorides **5**–**8** were determined by single-crystal X-ray diffraction.

10. **Hypervalent triorgano bismuthine, RBi(C$_6$F$_5$)$_2$ and racemic Bi-chiral diorganobismuth bromides R(C$_6$F$_5$)BiBr, R(Mes)BiBr, R(Ph)BiBr with the pendant arm ligand [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$]**,
A. M. Preda, C. I. Raţ, C. Silvestru, H. Lang, T. Rüffer and M. Mehring, *manuscript on final stage of preparation; to be submitted on May 2015.*

ABSTRACT: R(C$_6$F$_5$)$_2$Bi [R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$ (**1**)] was synthesized by reaction of RBiCl$_2$ with C$_6$F$_5$MgBr, or C$_6$F$_5$Li. The Bi-chiral bromides R(C$_6$F$_5$)BiBr (**2**), R(Mes)BiBr (**3**), and R(Ph)BiBr (**4**) were obtained from C$_6$F$_5$MgBr or MesMgBr and RBiCl$_2$ or from RLi and PhBiBr$_2$. The compounds were characterized by ^{1}H, ^{13}C NMR and mass spectrometry. The solid state structures of **1** - **4** were determined by single-crystal X-ray diffraction.

11. **A general route to monoorganopnicogen(III) (M = Sb, Bi) compounds with a pincer (N,C,N) group and oxo ligands**,
G. Strîmb, A. Pöllnitz, C. I. Raţ and C. Silvestru, *manuscript under evaluation at Dalton Transactions.*



ABSTRACT:

The reaction of $RMCl_2$ [R = 2,6-[MeN(CH_2CH_2)$_2$NCH_2]$_2$$C_6H_3$; M = Sb (**1**), Bi (**2**)] with KOH affords the isolation of the oxides *cyclo*-$R_2M_2O_2$ [M = Sb (**3**), Bi (**4**)]. Treatment of **3** with trifluoroacetic acid produced an ionic species (**5**) with a dinuclear cation that contains organic ligands protonated partially at one of the pendant arms. The cyclic oxide **3** is able to trap gaseous CO_2 to give "RSbCO_3" (**6**), the degree of oligomerization being under investigation. The reactivity of the dinuclear oxide **3** was also investigated towards oxalic acid or dopamine hydrochloride and pure mononuclear compounds could be isolated, *i.e.* RSb[O(O)CC(O)O] (**7**) and RSb[O_2-1,2-C_6H_3-3-(CH_2)$_2$$NH_3$]Cl (**8**). The reaction of the dichlorides **1** and **2** with ethylene glycol, pinacol or catechol, in presence of KOH, led to 2-organo-1,3,2-dioxastibolanes or -bismolanes RM(OCH_2)$_2$ [M = Sb (**9**), Bi (**10**)], RM($OCMe_2$)$_2$ [M = Sb (**11**), Bi (**12**)] and 2-organo-1,3,2-dioxastibole or -bismole RM(O_2-1,2-C_6H_4) [M = Sb (**13**), Bi (**14**)], respectively. The compounds were investigated by NMR spectroscopy, including variable temperature experiments, providing evidences for the presence of the intramolecular N→M interactions in solution. Single crystal X-ray diffraction studies were performed for most compounds and revealed an organic group R acting as a pincer ligand resulting in a distorted square pyramidal (*N*,*C*,*N*)MO_2 core with *cis* intramolecular N→M interactions placed in *trans* to M–O bonds. This contrasts to the N→M interactions *trans* to each other as found in the $RMCl_2$ used as starting materials. The crystals of the oxides **3** and **4**·4H_2O contain different geometric isomers with *trans* and *cis* orientation of the M–C bonds, respectively, with respect to the planar M_2O_2 ring. In the supramolecular polymeric architecture established in the crystal of **4**·4H_2O an important finding is the experimental observation of water hexamer units with a [tetramer+2] structure (water molecules connected to opposite corners of a square water tetramer) fixed between 1D-chains of the type (*cis*-$R_2Bi_2O_2$·H_2O)$_n$ through additional hydrogen bonds to oxygen atoms of the dinuclear organobismuth(III) moieties. Theoretical calculations were carried out on **2-14** in order to bring insight in the stabilization energy brought by intramolecular coordination of the pendant arms, association degrees and formation energies of the organopnicogen compounds with chelating ligands.

12. **Synthesis and structural characterization of substituted phenols with m-terphenyl backbone, 2,4,6-$R_3C_6H_2OH$ (R = 2,4,6-$Me_3C_6H_2$, Me_5C_6)**,
A. B. Şolea, M. Olaru, C. Silvestru and C. I. Raţ,
Z. Naturforsch., B: Chem. Sci., **2015**, *70*, 77-81.
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Abstract: Substituted phenols with a *m*-terphenyl backbone 2,4,6-$R_3C_6H_2OH$ [R = 2,4,6-$Me_3C_6H_2$ (**1**), Me_5C_6 (**2**)] were synthesized using Kumada cross-coupling reactions between 2,4,6-$I_3C_6H_2OH$ and the corresponding Grignard reagent. Both compounds were structurally characterized in solution by ^{1}H and ^{13}C NMR spectroscopy and HRMS. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction.

Contributions to national and international conferences

C1. *Chiral hypervalent organoantimony(III) cations*,
A. M. Preda, H. Lang, T. Rüffer, M. Mehring, C. Silvestru,
at *The XXV International Conference on Organometallic Chemistry (ICOMC)*, Lisbon (Portugal), September 2-7, **2012** (poster).

C2. *Organometallic compounds - unusual species stabilized through intramolecular coordination*,
C. Silvestru,
at *A 9-a Sesiune de Comunicări Ştiinţifice Studenţeşti*, Universitatea Bucureşti, Bucureşti, May 17, **2013** (invited opening plenary lecture).

C3. *The use of hypervalent organoantimony(III) cations as catalysts in the Mannich reactions*,
A. M. Preda, C. Silvestru,
at *The international Symposium of The Romanian Catalysis Society, (RomCat2013)*, Cluj-Napoca, May 29-31, **2013** (oral presentation).

C4. *Organometallic compounds - unusual species stabilized through intramolecular coordination*,
C. Silvestru,
at *The 13th Edition of Timişoara's Academic Days*, Timişoara, June 13, **2013** (invited plenary lecture).

C5. *Main Group organometallics – from molecular species to inorganic polymers*,
C. Silvestru,
at *Iaşi's Academic Days – A XXIV-a Sesiune de Comunicări Științifice a Institutului de Chimie Macromoleculară „Petru Poni"*, October 3-5, **2013** (invited plenary lecture).

C6. *Chelated antimony(III) and bismuth(III) alkoxides*,
A. Pöllnitz, G. Strîmb, C. Silvestru,
at *The 5th EuCheMS Chemistry Congres*, Istanbul (Turkey), August 31 - Septembrie 4, **2014** (poster).

C7. *New hypervalent organoantimony(III) and -bismuth(III) compounds*,
I. Chircă, A. M. Preda, C. Silvestru,
at *A XXXIII Conferinţă Naţională de Chimie*, Căciulata, Octombrie 1-3, **2014** (poster).

C8. *Syntheses and structural characterization of organoantimony(III) compounds with 2-(Ph_2NCH_2)C_6H_4 and 2-[Mes(Me)NCH_2]C_6H_4 substituents*,
G. Strîmb, C. I. Raţ, C. Silvestru,
at *A XXXIII Conferinţă Naţională de Chimie*, Căciulata, Octombrie 1-3, **2014** (poster).

Project Director,

Prof. Dr. Cristian Silvestru